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The Refractive Indices of Ethyl Alcohol and Water Mixtures

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THE REFRACTIVE INDICES OF ETHYL ALCOHOL AND WATER MIXTURES

BY

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I N T R O D U C T I O N

The measurements of refractive indices of ethyl alcohol and water mixtures have been performed by several investigators, and their findings are published in the International Critical Tables.

Data of refractive indices are given for several temperatures, from 15°C to 30°C, and for concentrations of alcohol ranging from 0 to 100 percent. In spite of these seemingly numerous data, no satisfactory conclusion can be drawn as to the peculiar shape of refractive index-concentration curves and no comparison of these curves with each other can be made when measurements at the temperatures above 20°C are considered. This is mainly due to the fact that determinations of refractive indices above 20°C were not performed for the same range of alcohol concentrations; they were made by several investigators who had various purposes in view.

The work described in the following pages consists of measuring refractive indices of alcohol water mixtures at temperatures from 20°C to 35°C, each time for the same concentration of alcohol. An attempt is made to correlate the findings with some recent views on the theory of solutions and the structure of alcohol and of water molecules.

PART I - THEORETICAL

The refractive power of a molecule is an additive and constitutive property depending on the number and kinds of atoms present and on the way these atoms are linked together. The atomic refraction of carbon, for example, is modified by the presence in a molecule of single, double and triple bonds. Constitutive properties usually predominate in case of chemical compounds; additive properties in case of mixtures in which no reaction of any kind takes place. Alcohol and water mixtures do not follow an additive mixture rule, as can be expected from the fact that diminution in volume and liberation of heat take place in mixing.

According to theoretical considerations, an increase in density of a substance should cause an increase in refractive index, since the numerical value of a denominator in the equation: $n=\frac{v \sin i}{v_1 \sin r}$ becomes smaller while numerator remains constant (n=index of refraction, v=speed of light in the first medium, v_1= speed of light in the second medium, i=angle of incidence, r=angle of refraction). Specific refraction of a substance formulated by Gladstone and Dale and Lorentz and Lorentz is $r=\frac{n-1}{d}$ and $r=\frac{n^2-1}{n^2+2}\frac{1}{d}$ respectively, where r is specific refraction, n

is refractive index and d is density. Gladstone and Dale's equation is empirical while Lorenz and Lorentz' is based on the electromagnetic theory of light.

In measuring refractive index of alcohol and water mixtures an increase in concentration of alcohol per unit volume of solution causes a decrease in specific gravity of solution which should be accompanied by a decrease in refractive index. Experimental results, however, are contrary to this line of thought.

When refractive indices of alcohol and water mixtures were measured at 20, 25, 30 and 35 degrees centigrade, with the concentration of alcohol ranging from 0 to 96 percent by weight, it became evident from the curves plotted that, with increasing concentration of alcohol, refractive index also increases until it attains a certain maximum value. Further increase in concentration of alcohol is accompanied by decrease in refractive index. The values of refractive index for the same percent concentration of alcohol are greatest when measured at 20°C and smallest when measured at 35°C.

An explanation proposed by John Holmes[a], who obtained as a result of his experiments curves of similar

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a J. Chem. Soc. 95, 1919, (1909); 103, 2147, (1913)

shape, is that physical forces alone operate in solution.

Volume change as well as refraction of alcohol water mixtures are not additive properties. The maximum differences in refraction occur at exactly the same concentrations as the maxima for volume change. Holmes observes that deviation in refractive index from theoretical additive relation follows closely the change in volume.

Assuming that molecules are spherical in shape, they can be packed together more or less closely, depending on the number of molecules present and the magnitude of their radii.

In a binary mixture like alcohol and water, the forces acting between these liquids are, according to Holmes, those of repulsion rather than attraction. If contraction in volume occurs, it is because the change resulting from close packing of water and alcohol molecules is greater in magnitude than normal forces of repulsion. When close packing is at the maximum, the inter-molecular spaces are reduced to minimum, hence the contraction in volume is the greatest.

Molecular spaces of ethyl alcohol, calculated by Holmes, are 1.48 when compared to water, equal to 1. As the concentration of alcohol in water increases from 0 percent to 77 percent the close packing of molecules increases until it reaches maximum value. The interspaces being diminished cause the increase in refractive index. With further increase in concentration of alcohol, the close packing becomes probably smaller, hence the decrease in refractive index.

The volume ratio of the molecular spheres varies little with the temperature and is proportional to the differences in the coefficients of expansion of the liquids.

When specific refractions of alcohol-water mixtures are calculated with the aid of Lorenz and Lorentz formula: $r=\frac{n^2-1}{n^2+2}\frac{1}{d}$ (r=sp. refraction, n=refractive index, d=density), and also with the aid of additive mixture rule: $r=q_1xr_1+q_2xr_2$, p.30, (r=sp. refraction of the mixture, q_1=quantity of water, r_1=sp. refraction of water, q_2=quantity of alcohol, r_2=sp. refraction of alcohol), the values obtained agree very closely with each other, the greatest discrepancy being 0.001, p.30.

This additive relation of alcohol and water points to the existence of ideal solution in which no interaction of any kind takes place. Refractive index values, on the

other hand, which enter into calculations of specific refractions deviate considerably from additive relation, the greatest deviation occurring at about 45% alcohol, p.32-39.

Molecular association of alcohol due to unsaturated or secondary valence forces producing compounds in which electrons or hydrogen nuclei are shared is repudiated by Smyth[a] on the ground that such associated alcohol

$$H\text{-}O\overset{R}{\diagup} \rightarrow H\text{-}O\overset{R}{\diagup} \rightarrow H\text{-}O\overset{R}{\diagup} \rightarrow H\text{-}O\overset{R}{\diagup} \rightarrow \text{etc.}$$

should cause a decrease in molecular refraction; calculations show that attachment of a hydrogen nucleus to oxygen brings a considerable reduction in refraction in the following manner:

$$O^{=}\ 7;\ OH^{-}\ 5.10;\ OH_2\ 3.75;\ OH_3^{+}\ 3.04$$

Since the degree of association varies by mixing with another liquid, the change in concentration should be accompanied by variation in refraction which, however, is not detectable experimentally.

Association found in water, alcohol and other polar liquids is attributed by Smyth as due to dipole in-

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a C. P. Smyth: Dielectric Constants and Molecular Structure, The Chemical Catalog Co., Inc., 1931, New York.

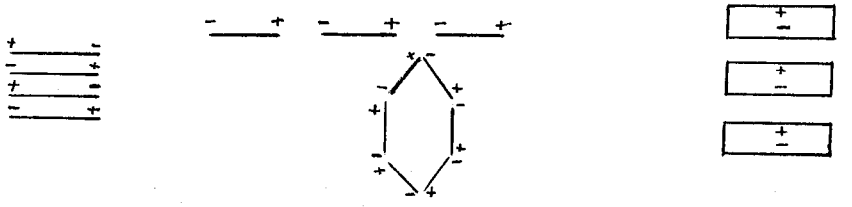
teraction without actual sharing of electrons between molecules. The quantitative expression of the interaction of molecular dipoles becomes very difficult, in view of the fact that effects of the dipoles upon one another depend not only upon their electric moments, but also upon the location of these moments in the molecules and upon the size and shape of molecules.

These effects of dipole interaction give evidence to the fact that when mixtures are investigated for different properties, they exhibit maxima and minima at different concentrations. In mixtures of polar molecules with non-polar, the non-polar molecules reduce the force acting between polar molecules and cause, for example, an increase in vapor pressure and reduction in viscosity. In mixtures of two polar liquids like alcohol and water, there is an interaction between molecules of the same kind and also of different kinds; and, therefore, the behavior of two polar liquids is not always the reverse of that between polar and non-polar. The properties of polar liquids may be influenced more by one kind of dipole interaction than by another, hence, various positions of maxima and minima.

The vapor pressure curve of alcohol and water is raised by mixing these liquids, probably because it is influenced mostly by attraction of alcohol and water

molecules, thus reducing forces acting between alcohol and alcohol, and water and water molecules. Viscosity and refractive index, on the other hand, are increased in alcohol water solutions because these properties are influenced by attraction of molecules of the same kind.

The relative orientation of dipoles is important in determining the behavior of mixtures. Some of the possible dipole orientations which determine the degree and the stability of molecular association are:



The shape and the size of molecules also play an important part in formation of molecular aggregates. Spherical molecules in which dipoles are more centrally located than in fibrillar molecules should exhibit smaller tendency to associate than the latter type.[a]

More recent work based on optical measurements throws light on the molecular structure of water and alcohol, and explains forces acting in solutions.

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a E. A. Hauser, Colloidal Phenomena, 1st Ed., p. 200, 1939, McGraw-Hill Book Company, Inc. New York

The structure of water as proposed by Bernal and Fowler[a] and further extended by Gibson[b] is based on X-ray and spectroscopic data which show each water molecule surrounded tetrahedrally by four other water molecules placed at a certain distance. Such arrangement is possible by assuming that each water molecule is a sphere with residual electrical charges at four points on the sphere which are situated at the vertices of a tetrahedron. Two of these charges are positive and two are negative. When spheres come in contact with each other, the positive poles of one touch the negative poles of another, thus building up a structure composed of a central molecule tetrahedrally surrounded by four neighbors. Such a structure is a very open one and contains a lot of empty spaces.

The addition of a substance to water will cause a change in the structure of the latter by influencing the residual charges and free intermolecular spaces. The nature of a molecule added and its size will determine either diminution or expansion in the free spaces and hence in volume. Polar substances will have a greater influence

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a J. Chem. Physics 1; 540,1933.

b Sci. Monthly 46, 103, (1938).

on the residual electrical charges of water than non-polar substances and this influence will again be modified by the size of a molecule, that is, by the closeness with which it can approach the empty spaces of water.

Alcohol molecule does not polarize water, and its large size does not permit a close approach to the free spaces, but alcohol by its bulk can break down the open structure of water, thereby, reducing the attractive forces between water molecules and causing contraction in volume. This contraction reaches a maximum value probably when all open structure units of water have been distorted. The influence of the further addition of alcohol upon structure can be attributed solely to the attractive forces acting between residual charges of water and alcohol, and to the association of alcohol molecules which increases in concentrated solutions.[a] This state of affairs is accompanied by diminution in volume smaller than the previous one.

Recent studies of the infra-red absorption of ethyl alcohol and water mixtures[b] reveal the presence of certain bonds which are not characteristic of either component of the mixture. The origin of these bonds is

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a Chem. Rev. 20, 257 (1937)

b J. Phys. Chem. 41, 645 (1937)

attributed to an interaction between the molecules of the components resulting either in the distortion of the water molecules or in association of water and alcohol molecules.

Refractive index data when referred to the above considerations are probably influenced by structural and polar characteristics of alcohol and of water molecules. The main factors present in the mixture are probably diminution in the free intermolecular spaces of water, interaction between alcohol and water, and association of alcohol. The first of these factors causes an increase in refractive index, and the last two cause a decrease in it. The net result corresponds to the influence which predominates. As the free spaces in water diminish, and the molecules become more closely packed, the refractive index increases until a maximum value corresponding to the disappearance of the open structure of water is reached. A further influence upon refraction is due to the attraction between water and alcohol molecules and to the association of alcohol. A picture of associated molecules determined by X-ray method[a] would indicate a rather open structure of molecular clusters formed by means of hydrogen bridge of

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a J. Am. Chem. Soc. 60,779,1938.

the hydroxyl group. Such a picture is in agreement with decreasing values in refractive index.

Some of the physical properties of alcohol and water (abnormal surface tension relationships, abnormal critical ratios, high latent heats of evaporation, high dielectric constants, and abnormal molecular weights in solution) studied by Sugden[a] give indication of association of alcohol and water, but data obtained do not measure the degree of association, and therefore have only a qualitative meaning.

Viscosity concentration curves of alcohol and water mixtures are similar to refractive index-concentration curves in that they show a maximum at a certain concentration. Explaining this maximum in viscosity, Dunstan[b] believes that association and eventually complex formation is greater at this point than at any other point. An examination of viscosity concentration curves shows that there is no appreciable shift of maximum with varying temperature. This indicates that aggregates which exist in solution posses a certain temperature range of stability. pp.18 and 19.

Jones,[c] on the other hand, believes that when

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a S. Sugden, The Parachor & Valency, 1930, Geo. Routledge and Sons, London

b J. Chem. Soc. 95, 1556 (1909)

c H. C. Jones, Conductivity & Viscosities in Pure and Mixed Solvents, 1915, Carnegie Institure of Washington, Washington, D. C.

two associated liquids are mixed, each diminishes the association of the other. The result is the formation of a large number of simple molecules from a smaller number of large complexes, with an increase of frictional surface and a consequent increase in viscosity.

A mechanism of viscous flow which takes account of empty spaces between molecules[a] is in better agreement with the structural picture of water-alcohol solution. When one layer of molecules slips over a neighboring layer of molecules, a double molecule, one from each layer, is instantaneously formed. If there is sufficient space available this double molecule can rotate and then dissociate. By a succession of these processes, one layer of liquid can flow past another layer.

It was calculated that, for many normal liquids, the activation energy for viscous flow is in the neighborhood of a third to a fourth the heat of vaporization. Since it requires the same energy to make a hole of molecular size as to vaporize a molecule, it was concluded that the required hole which permits rotation in viscous flow is about one-third to one-fourth the size occupied by a molecule.

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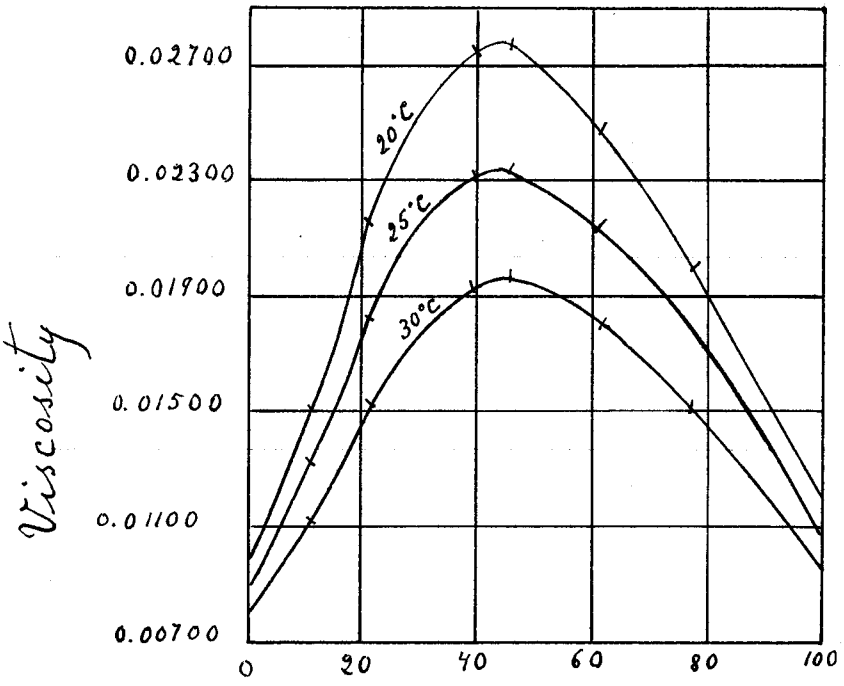
a J. Chem. Phys. 5, 907 (1937)

Destruction of open structure of water by addition of alcohol increases viscosity in accordance with above described mechanism. At about 45 percent alcohol (p.19) viscosity reaches maximum value which probably corresponds to the minimum space available for rotation to insure viscous flow.

Graph 1



From J. Chem. Soc. 95, 1556 (1909)

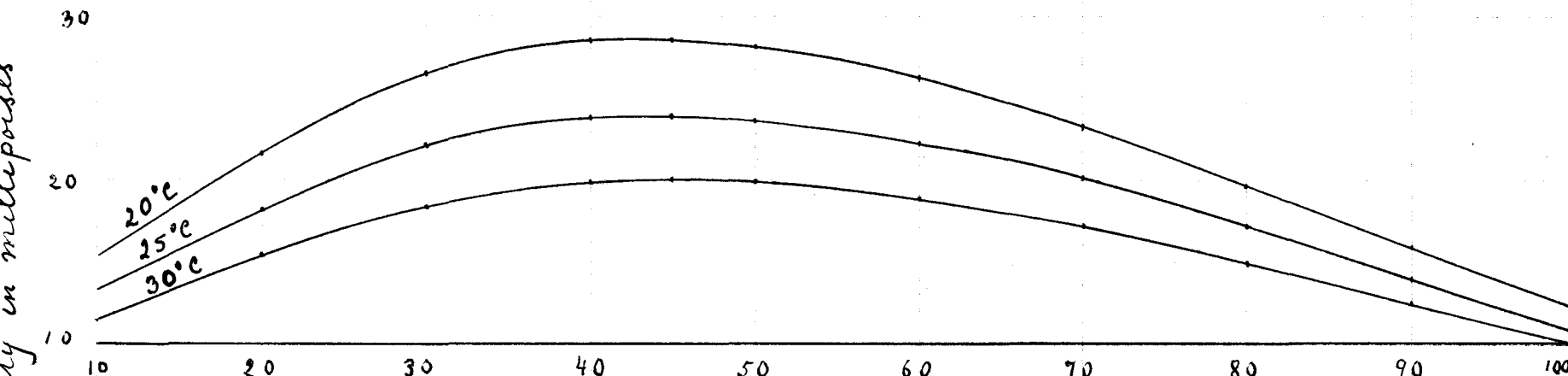
TABLE I

VISCOSITY OF ETHYL ALCOHOL-WATER SOLUTIONS

(Data from International Critical Tables.)

% of Alcohol by weight.	Viscosity in millipoises T=20°C	T=25°C	T=30°C
10	15.4	13.2	11.53
20	21.6	18.0	15.3
30	26.7	22.0	18.4
40	28.6	23.7	19.9
45	28.6	23.8	20.0
50	28.3	23.6	20.0
60	26.4	22.3	19.0
70	23.6	20.2	17.4
80	19.9	17.3	15.1
90	16.0	14.2	12.7
100	11.8	11.0	9.97

Graph 2



Percent of ethyl alcohol by weight

Data from International Critical Tables

PART II - EXPERIMENTAL

In obtaining data which follow, samples of ethyl alcohol were diluted with distilled water to approximately desired concentrations. Densities of these solutions were determined in a pyknometer bottle at a constant temperature regulated by automatically controlled thermostat. The exact concentrations of the sample solutions were then calculated from the densities. Refractive index measurements were accomplished with an Abbé refractometer at four temperatures: 20°C, 25°C, 30°C and 35°C. These temperatures were maintained constant by letting a stream of water from the thermostat circulate through water jackets in which the prisms of the refractometer are mounted.

The greatest possible accuracy attainable in the refractometer used is 0.0001. The five decimal figures which appear in the tables are the average values of seven readings taken each time. The last decimal figures do not appear, however, in the graphs.

The refractive index values for the same percent concentration of alcohol are highest when measured at 20°C and lowest when measured at 35°C. The maximum values at 20°C, 25°C, 30°C and 35°C are respectively: 1.36490, 1.36341, 1.36116 and 1.35913. At 20°C the maximum in re-

fractive index corresponds to 82.86% alcohol (p.23). At 25°C maximum occurs at lower concentration, namely, 77.01% (p.25); at 30°C maximum is at 77.35% (p.27), and at 35°C, it is again at 82.86% (p.29).

In the last two instances, i.e., at 30°C and 35°C, the maxima in refraction were chosen on the basis of the fifth decimal figure. However, if four decimal figures are considered, maximum in refraction possesses a certain range of stability extending from 77.35% to 82.86%. At these concentrations of alcohol, the refractive index values are the same, namely, 1.3611 at 30°C (p.26,27) and 1.3591 at 35°C (p.28,29).

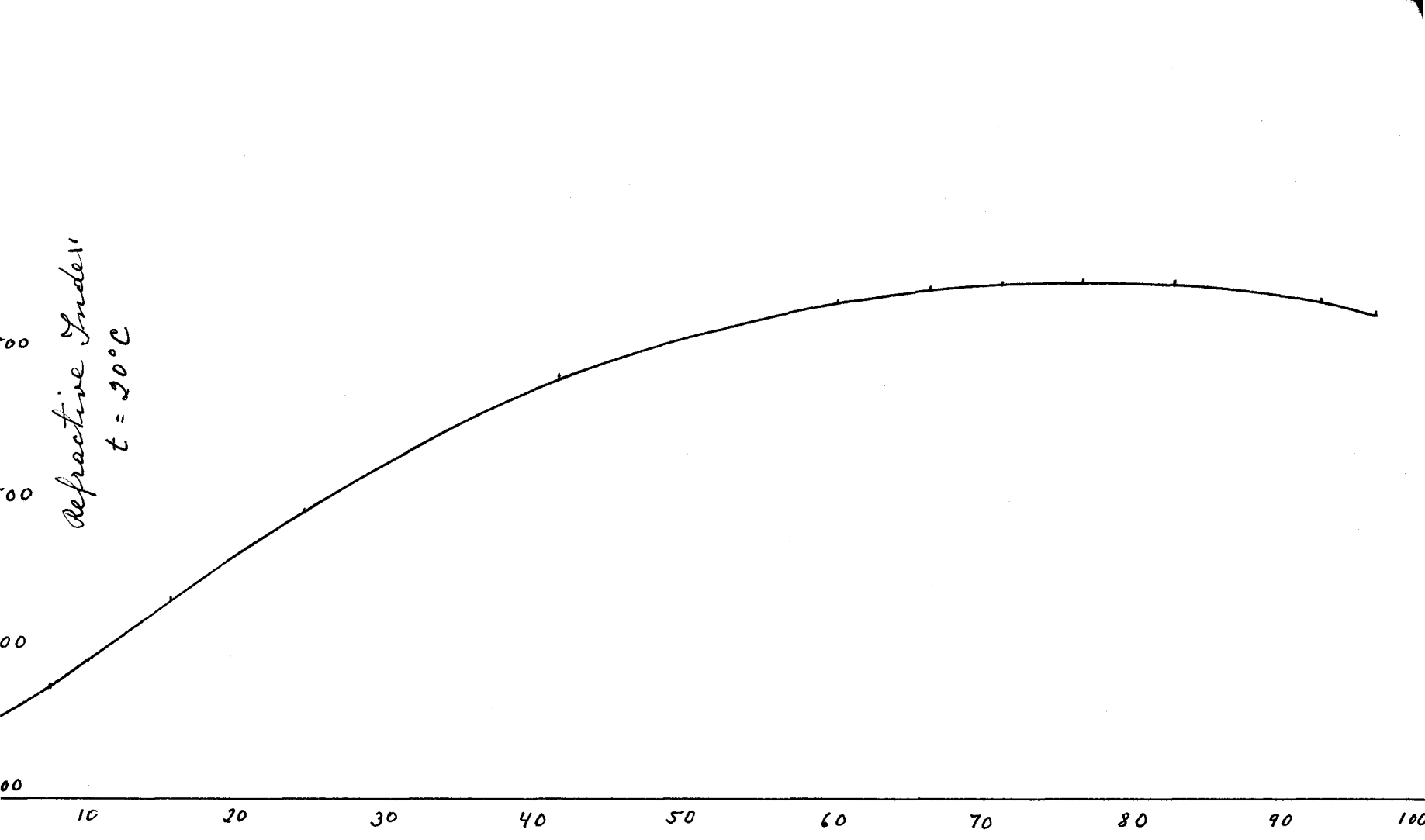
All four refractive index-concentration curves have similar shapes in that they rise rapidly with increasing concentration up to about 70%. Past this concentration, they approach the maximum point slowly and then drop rather rapidly. The tables and the accompanying curves are shown on pp.22-29 .

TABLE II

Refractive Index of Ethyl Alcohol-Water Mixtures at 20°C

% of Ethyl Alcohol by weight.	Refractive Index T 20°C
0.00	1.33316
7.61	1.33795
15.55	1.34362
24.42	1.34914
41.51	1.35856
60.45	1.36336
66.44	1.36410
71.23	1.36462
77.35	1.36476
82.86	1.36490
83.55	1.36486
92.68	1.36370
96.33	1.36237

Maximum = 1.36490 at 82.86%.


Refractive Index
t = 20°C
00
00
00
00
10
20
30
40
50
60
70
80
90
100
Percent of ethyl alcohol by weight
Maximum at 82.86 %

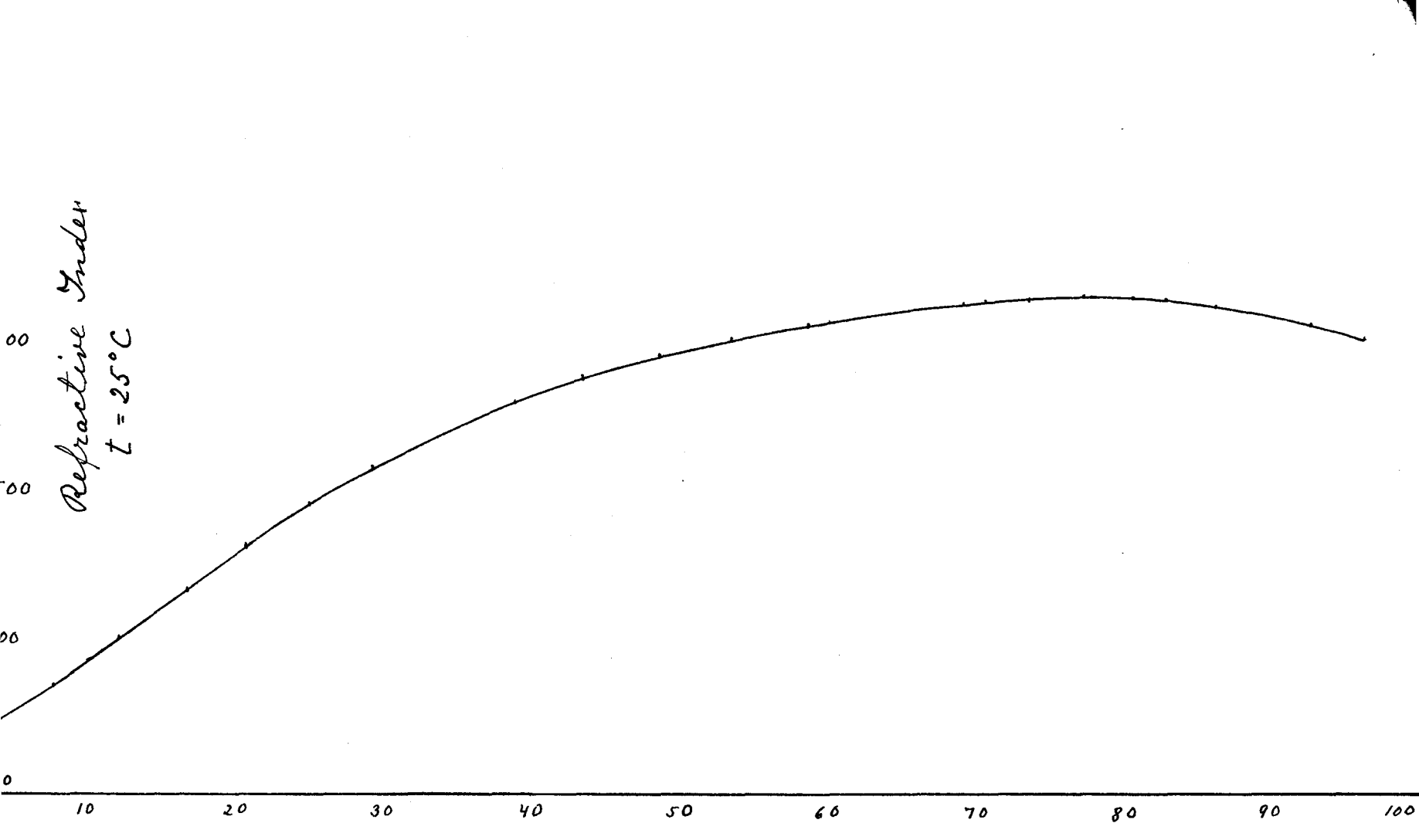
Graph 3

TABLE III

Refractive Index of Ethyl Alcohol-Water Mixtures at 25°C

% of Ethyl Alcohol by Weight.	Refractive Index T 25°C	% of Ethyl Alcohol by Weight.	Refractive Index T 25°C
0.00	1.33276	70.40	1.36304
3.96	1.33505	73.67	1.36319
7.61	1.33720	74.11	1.36321
8.02	1.33763	75.86	1.36334
12.04	1.34068	77.01	1.36341
16.45	1.34364	78.32	1.36339
20.46	1.34678	79.39	1.36331
25.04	1.34965	80.57	1.36327
29.41	1.35188	81.30	1.36325
38.82	1.35630	82.88	1.36314
43.67	1.35795	83.81	1.36307
48.49	1.35940	84.81	1.36301
53.60	1.36075	86.07	1.36292
58.49	1.36160	92.68	1.36166
60.45	1.36185	96.33	1.36083
69.10	1.36298		

Maximum = 1.36341 at 77.01%


Refractive Index
t = 25°C
00
00
00
0
10
20
30
40
50
60
70
80
90
100
Percent of ethyl alcohol by weight
Maximum at 77.01 %

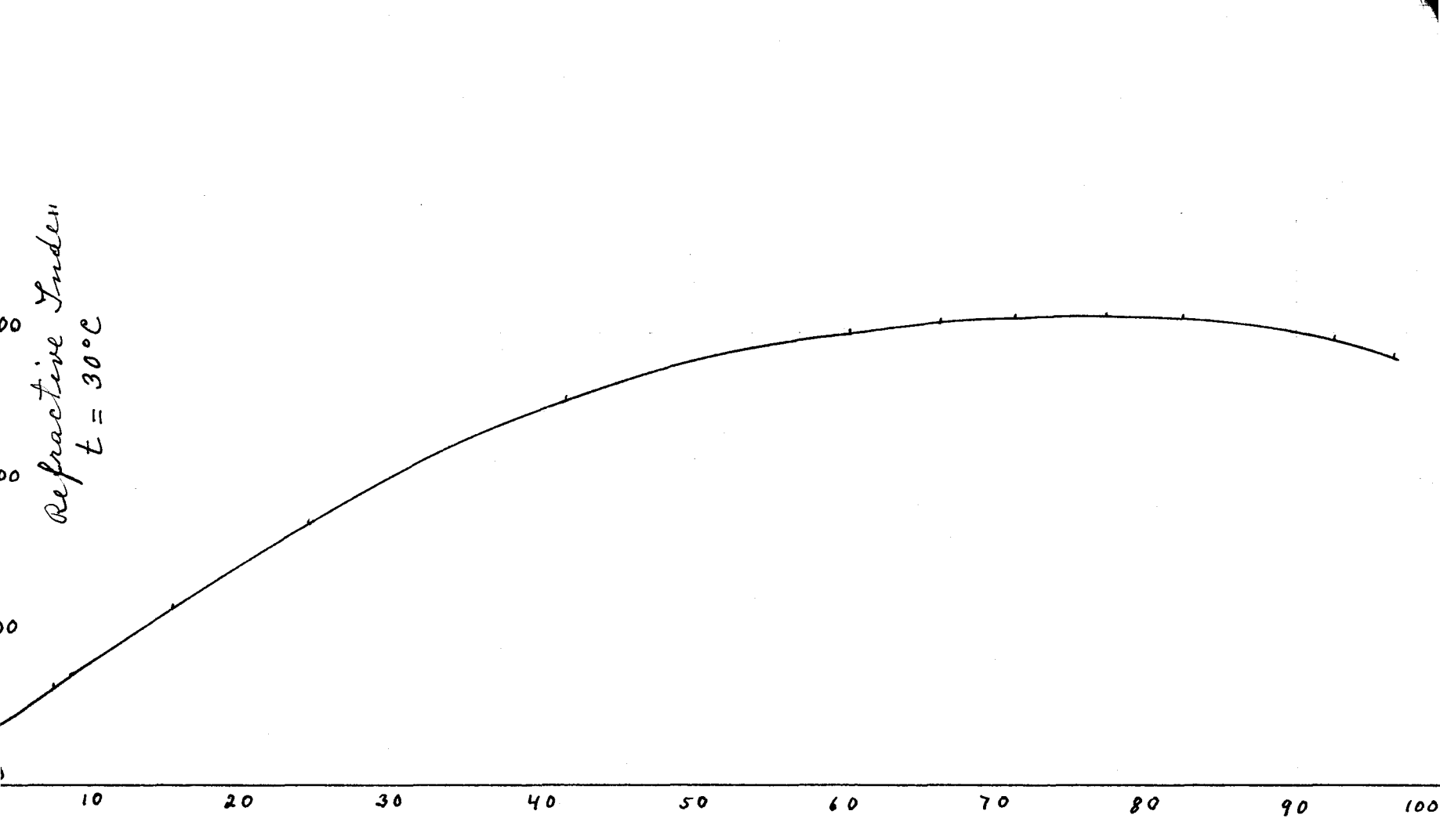
Graph 4

TABLE IV

Refractive Index of Ethyl Alcohol-Water Mixtures at 30°C

% of Ethyl Alcohol by weight.	Refractive Index T 30°C
0.00	1.33178
7.61	1.33658
15.55	1.34188
24.42	1.34715
41.51	1.35580
60.45	1.35992
66.44	1.36060
71.23	1.36104
77.35	1.36116
82.86	1.36113
83.55	1.36098
92.68	1.35963
96.33	1.35835

Maximum = 1.36116 at 77.35%.



Percent of ethyl alcohol by weight

Maximum at 77.35%

Graph 5

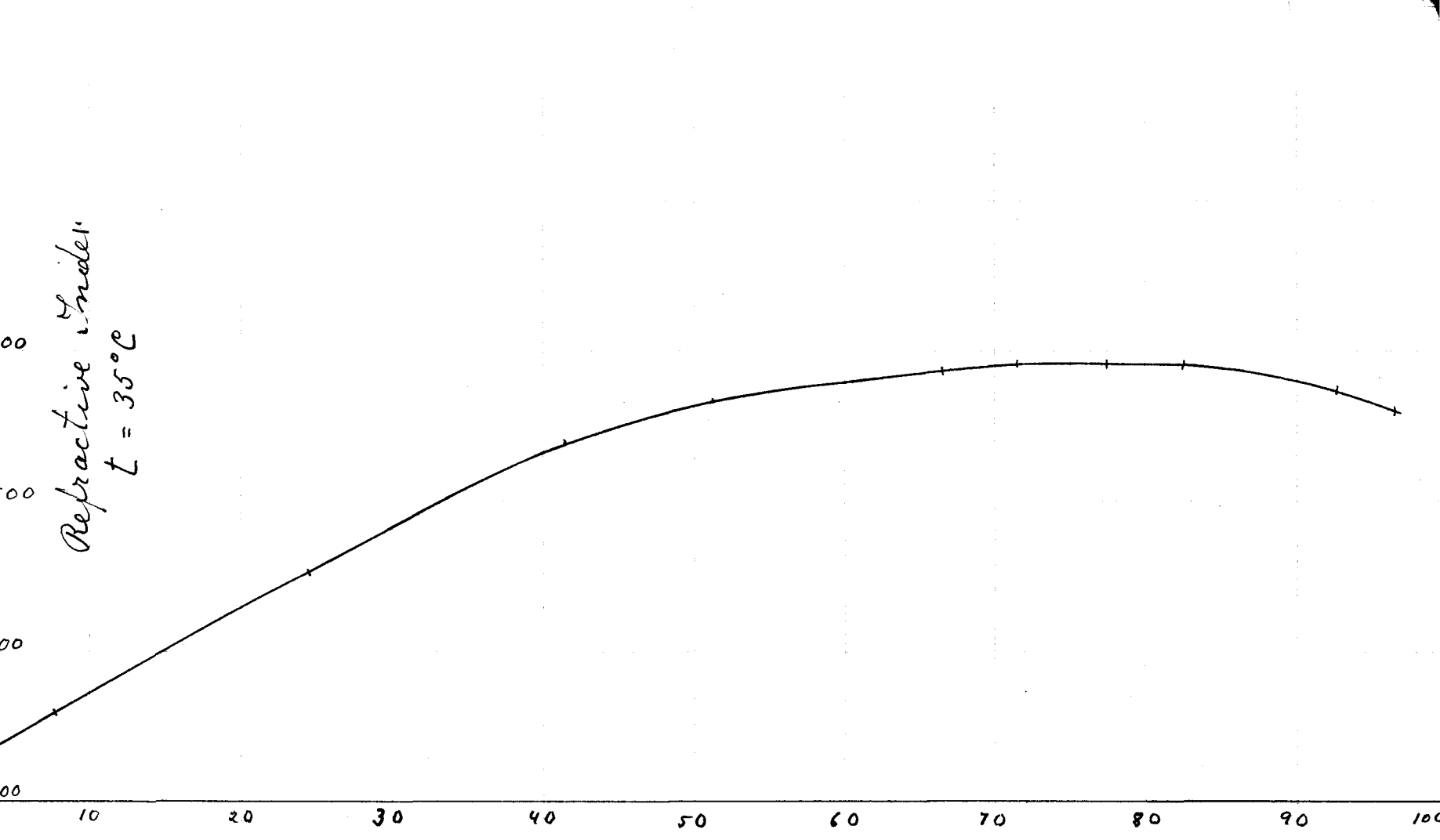
17

TABLE V

Refractive Index of Ethyl Alcohol-Water Mixtures at 35°C

% of Ethyl Alcohol by weight.	Refractive Index T 35°C
0.00	1.33174
7.61	1.33600
24.42	1.34502
41.51	1.35404
60.45	1.35811
66.44	1.35880
71.23	1.35908
77.35	1.35911
82.86	1.35913
83.55	1.35901
92.68	1.35760
96.33	1.35600

Maximum = 1.35913 at 82.86%



Percent of ethyl alcohol by weight
Maximum at 82.86%

Graph 6

TABLE VI

SPECIFIC REFRACTIONS OF ALCOHOL-WATER MIXTURES

-I-	-II-	-III-	-IV-
% of ethyl alcohol by weight.	Sp. refractions calculated with aid of Lorenz & Lorentz equation: $r = \frac{n^2-1}{n^2+2}\frac{1}{d}$	Sp. refractions calculated with aid of additive mixture rule: $r = q_1r_1+q_2r_2$	Difference between 2 & 3
0.00	0.2061	0.2061	0.0000
3.69	0.2089	0.2082	0.0007
7.61	0.2114	0.2117	0.0003
8.02	0.2118	0.2120	0.0002
12.04	0.2147	0.2150	0.0003
16.45	0.2178	0.2183	0.0005
20.46	0.2209	0.2213	0.0004
25.04	0.2243	0.2248	0.0005
29.41	0.2271	0.2280	0.0009
38.82	0.2341	0.2350	0.0009
43.67	0.2376	0.2386	0.0010
48.49	0.2413	0.2422	0.0009
53.60	0.2451	0.2460	0.0009
58.49	0.2489	0.2497	0.0008
60.45	0.2502	0.2511	0.0009
69.10	0.2568	0.2576	0.0008
70.43	0.2578	0.2586	0.0008
73.67	0.2602	0.2610	0.0008
74.11	0.2606	0.2613	0.0007

TABLE VI
(continued)

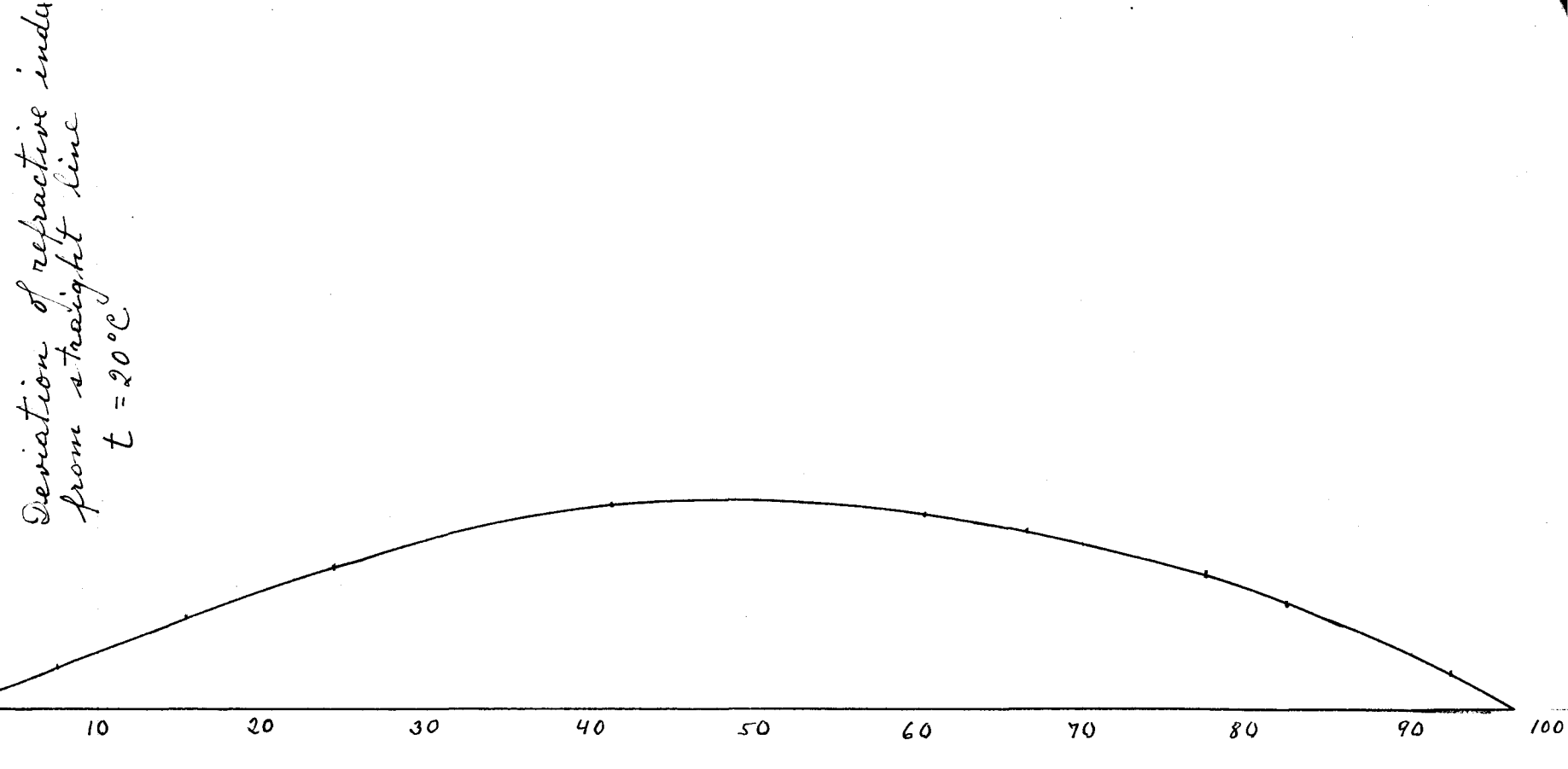
-I- % of ethyl alcohol by weight.	-II- Sp. refractions calculated with aid of Lorenz & Lorentz equation: $r = \frac{n^2-1}{n^2+2}\frac{1}{d}$	-III- Sp. refractions calculated with aid of additive mixture rule: $r = q_1 r_1 + q_2 r_2$	-IV- Difference between 2 & 3
75.86	0.2620	0.2626	0.0006
77.01	0.2629	0.2635	0.0006
78.32	0.2639	0.2645	0.0006
79.39	0.2647	0.2653	0.0006
80.57	0.2655	0.2661	0.0006
81.30	0.2661	0.2667	0.0006
82.88	0.2673	0.2679	0.0006
83.81	0.2680	0.2687	0.0007
84.81	0.2688	0.2693	0.0005
86.07	0.2699	0.2702	0.0003
92.68	0.2748	0.2752	0.0004
96.33	0.2778	0.2779	0.0001
100.	0.2807	0.2807	0.0000

TABLE VII

DEVIATION OF REFRACTIVE INDEX
from
ADDITIVE RELATION

(Calculated from Graph III)

% ethyl alcohol by weight.	Refractive Index T 20°C	Deviation
7.61	1.33790	0.0024
15.55	1.34362	0.0058
24.42	1.34914	0.0088
41.51	1.35856	0.0127
60.45	1.36336	0.0118
66.44	1.36410	0.0108
71.23	1.36462	0.0098
77.35	1.36476	0.0083
82.86	1.36490	0.0067
83.55	1.36486	0.0064
92.88	1.36370	0.0025


Deviation of refractive index
from straight line
t = 20°C
10
20
30
40
50
60
70
80
90
100
Percent of ethyl alcohol by weight

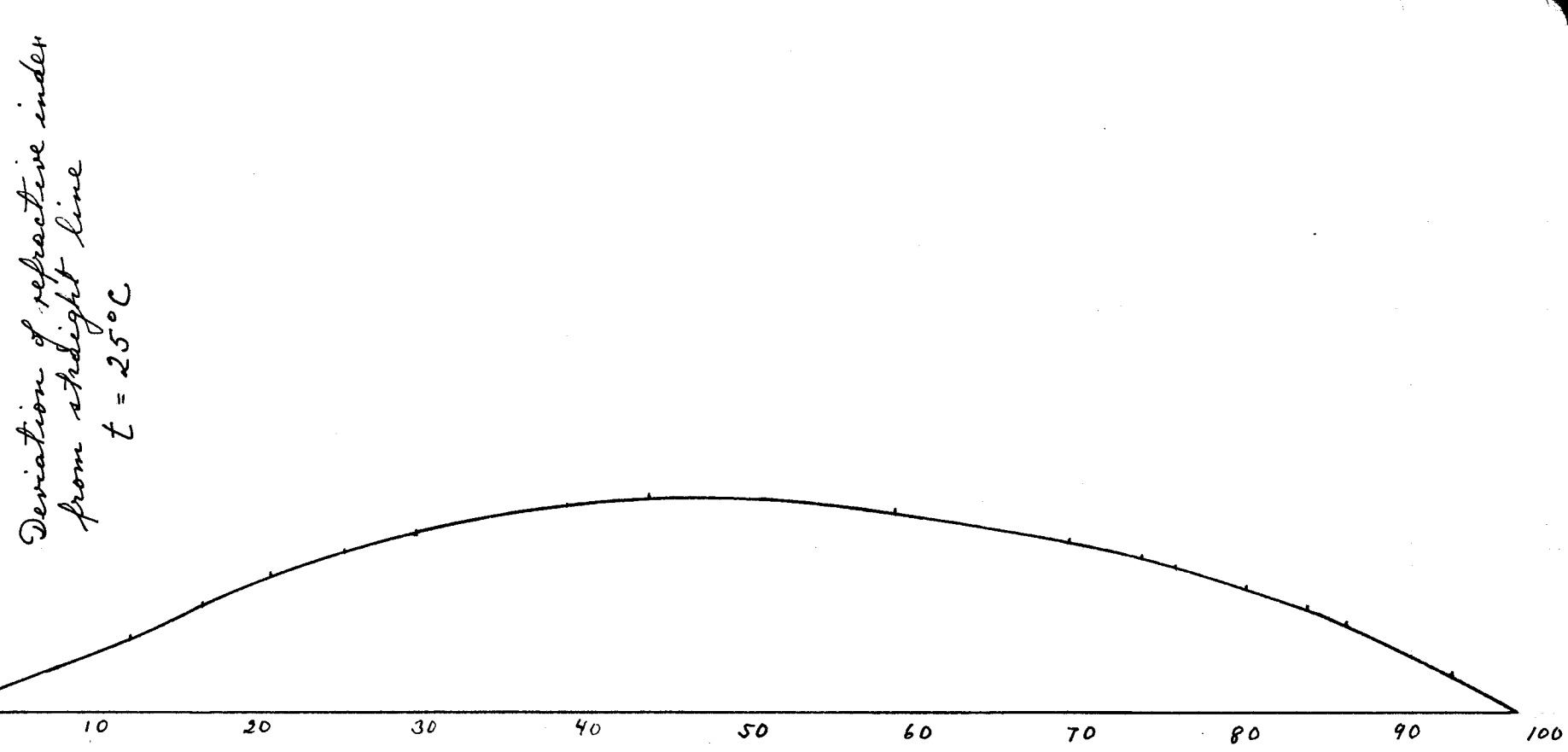
Graph 7

TABLE VIII

DEVIATION OF REFRACTIVE INDEX from ADDITIVE RELATION

(Calculated from Graph IV)

% ethyl alcohol by weight.	Refractive Index T 20°C	Deviation
3.96	1.33505	0.0014
7.61	1.33720	0.0025
12.04	1.34068	0.0046
16.45	1.34364	0.0063
20.46	1.34678	0.0083
25.04	1.34965	0.0098
29.41	1.35188	0.0108
38.82	1.35630	0.0126
43.67	1.35795	0.0131
48.49	1.35940	0.0129
53.60	1.36075	0.0126
58.49	1.36160	0.0122
69.10	1.36298	0.0103
73.67	1.36319	0.0093
75.86	1.36334	0.0087
77.01	1.36341	0.0086
79.39	1.36331	0.0077
83.81	1.36307	0.0062
86.07	1.36292	0.0054
92.68	1.36166	0.0022


Deviation of refractive index from straight line
t = 25°C
10
20
30
40
50
60
70
80
90
100
Percent of ethyl alcohol by weight

Graph 8

TABLE IX

DEVIATION OF REFRACTIVE INDEX
from
ADDITIVE RELATION

(Calculated from Graph V)

% ethyl alcohol by weight.	Refractive Index T 30°C	Deviation
7.61	1.33658	0.0029
15.55	1.34188	0.0061
24.42	1.34715	0.0090
41.51	1.35580	0.0130
60.45	1.35992	0.0119
66.44	1.36060	0.0108
71.23	1.36104	0.0099
77.35	1.36116	0.0083
82.86	1.36113	0.0063
92.68	1.35963	0.0024

Graph 9

Percent of ethyl alcohol by weight
10
20
30
40
50
60
70
80
90
100
Deviation of refractive index from straight line
t = 30°C

TABLE X

DEVIATION OF REFRACTIVE INDEX
from
ADDITIVE RELATION

(Calculated from Graph VI)

% ethyl alcohol by weight.	Refractive Index T 35°C	Deviation
7.61	1.33600	0.0026
15.55	1.34125	0.0053
24.42	1.34502	0.0066
41.51	1.35404	0.0108
60.45	1.35811	0.0096
66.44	1.35880	0.0086
71.23	1.35908	0.0076
77.35	1.35911	0.0059
82.86	1.35913	0.0045
83.55	1.35901	0.0043
92.68	1.35760	0.0024

Graph 10

Percent of ethyl alcohol by weight
10
20
30
40
50
60
70
80
90
100
Variation of refractive index
from standard line
t = 35°C

Comparing refractive index concentration curves with those plotted on the basis of data found in the International Critical Tables (p. 43,44) it is seen that they are similar in shape and possess a certain temperature range of stability. Data below show that within the range of 20 degrees centigrade (35°C - 15°C) the maximum in refractive index oscillates within the limits of alcohol concentration equal to 6.74% (83.75% - 77.01%); the values for refractive index decrease with increasing temperature.

Data from International Critical Tables

T°C	% of Ethyl Alcohol by weight corresponding to maximum	Refractive Index maximum
15	80	1.36690
15.5	83.63	1.36651
17.5	83.75	1.36587
20	79.4	1.36500
25	79.3	1.363315
	Data from Tables II, III, IV, V	
20	82.86	1.36490
25	77.01	1.36341
30	77.35	1.36116
35	82.86	1.35913

In view of the preceding discussion, a temperature range of stability would indicate that a similar internal structure of alcohol-water mixtures exists within

this range and refraction becomes proportional to the thermal expansibility of liquids. At higher temperatures where kinetic effects might be very great, the structural composition of the mixture should become different. The deviation from a straight line function for temperatures measured is greatest at about 45 percent alcohol and does not change appreciably within limited temperature range.

From the effects of pressure (p. 46,47), it is seen that the composition of alcohol-water mixtures at the minimum boiling point varies with pressure; the composition of alcohol decreasing with increasing pressure. This seems to indicate that no definite compound formation is present. As pressure is increased, the attraction between alcohol molecules becomes probably greater than between alcohol and water molecules and the escaping tendency of alcohol becomes smaller.

This pressure effect together with viscosity and refractive index data gives support to the hypothesis of dipole interaction and formation of unstable continuous polar lattices by alcohol and water molecules.

A view taken by Marsh[a] is that substances which exhibit negative deviation from Raoult's law, possess ten-

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a J. S. Marsh, Principles of Phase Diagrams, 1st Ed., 1935, McGraw-Hill Book Company, Inc., New York.

dency toward compound formation. Although no definite compounds can be isolated, the interaction of dipoles is sufficient to establish equilibrium between substances A and B, $A + B \rightleftarrows AB$. Such reactions are accompanied by an energy change which manifests itself as heat energy, which may be regarded as heat of reaction. The fact that composition of solutions varies with pressure does not exclude the tendency to form compounds. Marsh has shown that positions of maxima and minima depend entirely upon the "tilt" of the curve. When deviation curve is rotated in such a way that the perfect solution straight line is in horizontal position, the maximum and minimum values for a given property correspond to new mol fraction values of solution.

Viscosity and refractive index data together with pressure effect, give support to the hypothesis of dipole interaction which results either in formation of unstable continuous polar lattices by alcohol and water molecules, or in a stable equilibrium condition existing between associated and unassociated molecules.

TABLE XI

REFRACTIVE INDEX OF ETHYL ALCOHOL-WATER MIXTURES

(From International Critical Tables)

% ethyl alcohol by wt. T 15°C	Refractive Index	% ethyl alcohol by wt. T 17.5°C	Refractive Index	% ethyl alcohol by wt. T 20°C	Refractive Index
0	1.33345	0	1.33320	2.2	1.3333
10	1.34020	0.99	1.33367	2.8	1.3335
20	1.34778	1.80	1.33416	3.92	1.3341
30	1.35420	2.60	1.33466	8.04	1.3370
40	1.35948	3.41	1.33517	16.33	1.3432
46	1.36170	4.22	1.33568	24.49	1.3492
50	1.36290	8.32	1.33843	33.35	1.3545
55	1.36405	16.25	1.34441	42.4	1.3585
60	1.36505	26.31	1.35043	52.09	1.3615
65	1.36586	35.67	1.35565	62.6	1.3633
70	1.36645	45.27	1.35953	73.7	1.3648
75	1.36676	55.42	1.36248	79.4	1.3650
80	1.36690	66.05	1.36448	85.8	1.3643
85	1.36678	77.21	1.36565	92.5	1.3635
90	1.36626	83.75	1.36587	99.3	1.3618
95	1.36518	88.46	1.36565		
100	1.36332	95.04	1.36448		
		100.	1.36229		

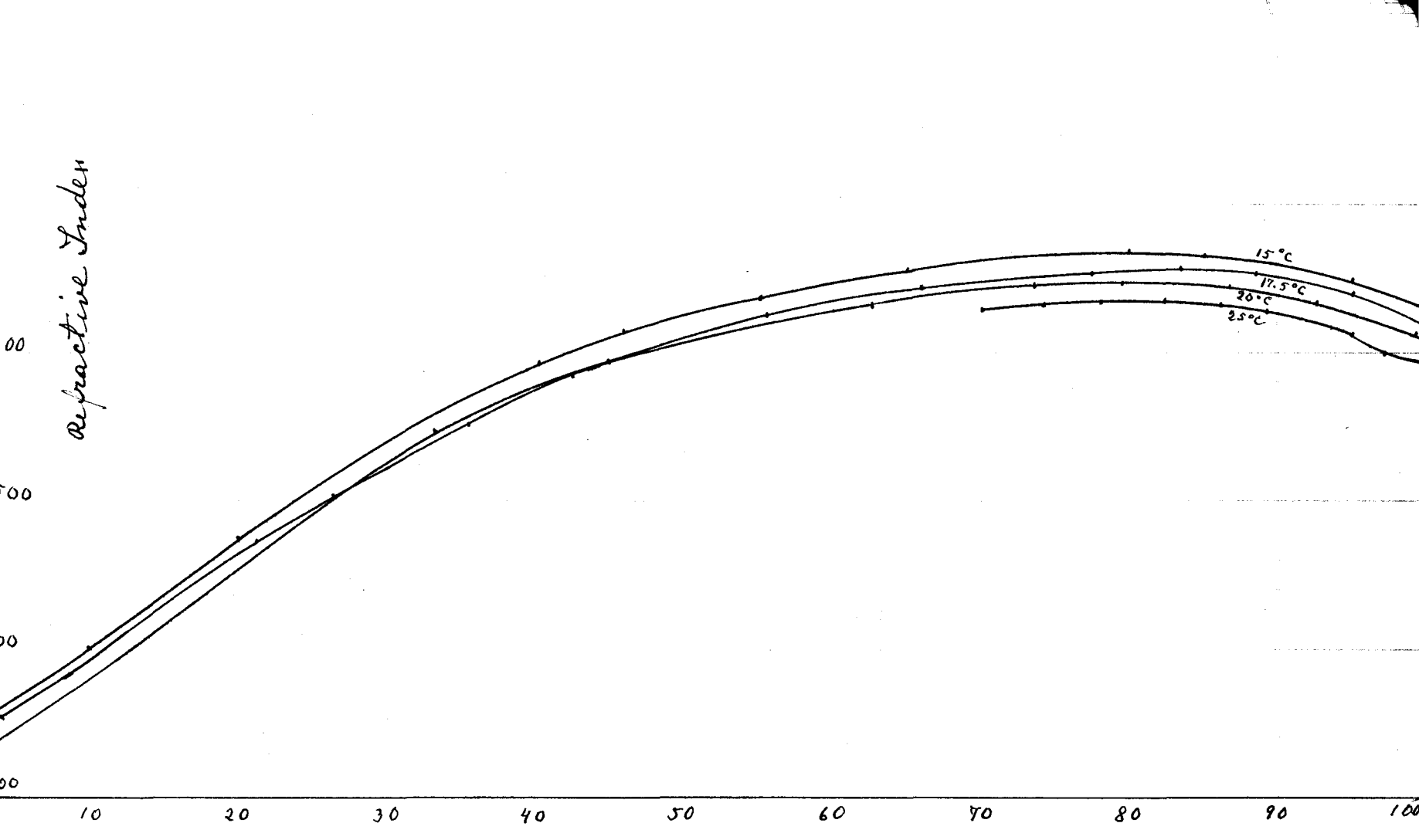
TABLE XI

REFRACTIVE INDEX OF ETHYL ALCOHOL-WATER MIXTURES

(From International Critical Tables)

(Continued)

% ethyl alcohol by wt. T 25°C	Refractive Index	% ethyl alcohol by wt. T 25°C	Refractive Index
70	1.363038	87	1.36280
74	1.363208	88	1.36269
75	1.363239	89	1.36255
76	1.363265	90	1.36239
77	1.363286	91	1.36221
78	1.363302	92	1.36200
79	1.363313	93	1.36178
79.3	1.363315	94	1.36153
80	1.36331	95	1.36125
81	1.36326	96	1.36094
82	1.36319	97	1.36061
83	1.36312	98	1.36024
84	1.36305	99	1.35984
85	1.36297	100	1.35941
86	1.36290		



Percent of ethyl alcohol by weight

Data from International Critical Tables

Graph 11

45

TABLE XII

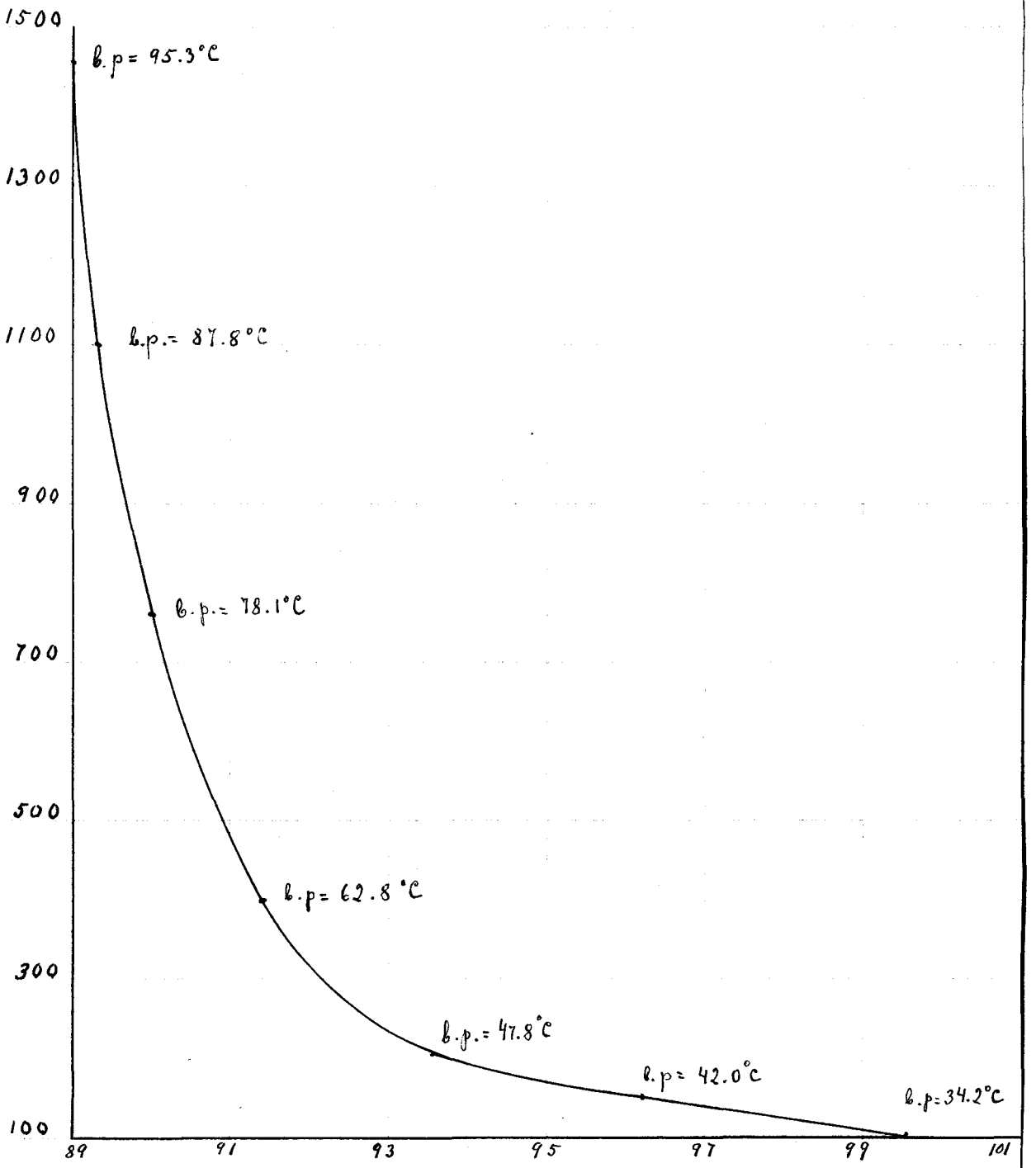
EFFECT OF PRESSURE UPON AZEOTROPIC MIXTURES

(From International Critical Tables)

A = H_2O B = C_2H_5OH

p. mm Hg	B.P. °C	Mol % B
100	34.2	99.6
150	42.0	96.2
200	47.8	93.8
400	62.8	91.4
760	78.1	90.0
1100	87.8	89.3
1450	95.3	89.0

Graph 12


1500
1300
1100
900
700
500
300
100
Pressure in mm. Hg
b.p = 95.3°C
b.p.= 87.8°C
b.p.= 78.1°C
b.p = 62.8 °C
b.p.= 47.8°C
b.p = 42.0°C
b.p=34.2°C
89
91
93
95
97
99
101
Mol percent of alcohol at minimum boiling points

C O N C L U S I O N

Taking into consideration errors in observation and measurements, the general shape of refractive index-composition curves determined in this work compares favorably with refractive index values for lower temperatures tabulated in the International Critical Tables.

Recent researches in the realm of pure liquids and solutions indicate an importance of the structural effects present in liquids. Physical properties become thus a function of structural modifications which accompany pure liquids and solutions.

In the light of older theories, these structural modifications were due only to physical forces. Recent views, on the other hand, take account of both physical and chemical forces mainly through the interaction of dipoles.

The interpretation of refractive index values of alcohol and water mixtures was attempted in the light of both theories. In the first instance, refractive index becomes a function of relative magnitudes of molecular volumes of alcohol and water, and relative number of different molecular species present. The resultant effect is a greater or smaller diminution in the free intermolecular spaces between alcohol and water molecules.

In the second instance, refractive index does not

depend only on the size and shape of molecules, but also on the polar character of water and alcohol. The interaction of dipoles present in these liquids accounts for their association, the degree of which varies with the change in concentration. Refractive index as well as other physical properties become directly influenced by interaction of dipoles between molecules of the same species and between molecules of different species.

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The thesis, "The Refractive Indices of Ethyl Alcohol and Water Mixtures," written by Janina Nowakowska, has been accepted by the Graduate School with reference to form, and by the readers whose names appear below, with reference to content. It is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

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